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(54) PROCESS FOR THE PREPARATION OF STABLE POLYCARBODIIMIDE DISPERSIONS IN WATER, WHICH ARE FREE OF ORGANIC SOLVENTS AND MAY BE USED AS CROSSLINKING AGENT

VERFAHREN ZUR HERSTELLUNG STABILER , WÄSSRIGER POLYCARBODIIMIDDISPERSIONEN, DIE KEINE ORGANISCHEN LÖSUNGSMITTEL ENTHALTEN UND GEEIGNET SIND, UM ALS VERNETZUNGSMITTEL VERWENDET ZU WERDEN

PROCEDE DE PREPARATION DE DISPERSIONS DE POLYCARBODIIMIDE STABLES DANS L'EAU, DEPOURVUES DE SOLVANTS ORGANIQUES ET POUVANT ETRE UTILISEES EN TANT QU'AGENT DE RETICULATION

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Description

[0001] Polycarbodiimides are well known crosslinking agents for aqueous resins containing carboxylic acid functions. Most commercially available polycarbodiimide crosslinkers are dissolved in an organic solvent, which is disadvantageous for environmental reasons. Further, they have to be mixed with either water, or water and a surfactant, before they can be mixed with the aqueous resin. Generally, these aqueous dispersions are not stable and have to be freshly prepared daily. Only aqueous tetramethylxylene diisocyanate based polycarbodiimides are stable in water as described in US 5688875 (=EP 0686626) and US 5859166. However, a disadvantage of these polycarbodiimides is that the conditions for the carbodiimide formation from tetramethylxylene diisocyanate are rather extreme: 22 hrs at 180°C are required and 2 % of a carbodiimide catalyst. Further tetramethylxylene diisocyanate based polycarbodiimides are slower and less efficient crosslinkers than isophorone diisocyanate or 4,4'-dicyclohexylmethane diisocyanate based crosslinkers.

[0002] Aqueous polycarbodiimide dispersions obtained from isophorone diisocyanate and from 4,4'-dicyclohexylmethane diisocyanate as described in US 5856014, US 5958516, US 6127029, US 6127477, are not stable. The carbodiimide amounts from commercial aqueous polycarbodiimide products (Carbodilites from Nisshinbo Industries) decrease in a stability test at 50° within 6 weeks to 15-70 % of the original value.

[0003] US 6 248 819 B1 and EP 0 686 626 both disclose the preparation of hydrophilized polycarbodiimid crosslinkers.

[0004] The object of the present invention is to provide a process in which the disadvantages mentioned above are eliminated.

Description of the invention

[0005] According to the present invention there is provided a process for the preparation of stable aqueous polycarbodiimide dispersions, to be used as crosslinking agent, which are free of organic solvents, characterised in:

- reacting a polyisocyanate in the presence of a carbodiimide catalyst to form a polycarbodiimide,
- terminating and/or chain extending the polycarbodiimide chain by the addition of a compound containing a hydrophilic group and one or more amine and/or hydroxy functions during or after the polycarbodiimide formation,
- dispersion of the resulting compound in water,
  wherein the pH is adjusted between 11 and 14 by the addition of a base or a buffer to the water used for the dispersion and/or to the obtained aqueous dispersion. Alternatively stable aqueous polyisocyanate based polycarbodiimide dispersions can be obtained when the capping or chain extension with the compound containing a hydrophilic group and one or more amine functions is not effected during or after the polycarbodiimide formation, but occurs during or after the dispersion of the polycarbodiimide in water.

[0006] Surprisingly the stability of the polycarbodiimide dispersions was significantly increased at higher pH values and the carbodiimide concentration was not decreased within 8 weeks at 50°C. Preferrably at the end of the process the pH will be adjusted to a value between 11 and 13.

[0007] Conventional carbodiimide catalysts as described in EP 878496 may be used. Surprisingly, it appeared that the reaction temperature and the reaction time could be reduced when 1-methylphospholene-1-oxide was used as catalyst and for this reason this catalyst is preferred.

[0008] The polyisocyanate which is used to prepare the polycarbodiimide is a conventional polyisocyanate and may be toluene-2,4-diisocyanate, toluene-2,6- diisocyanate and mixtures thereof, diphenylmethane-4,4-diisocyanate, 1,4-phenylenediisocyanate, dicyclohexylmethane-4,4'diisocyanate, 3-isocyanatomethyl-3,5,5trimethylcyclohexylisocyanate, 1,6-hexyldiisocyanate, 1,4-cyclohexyl-diisocyanate, norbonyldiisocyanate diisocyanate, or a mixture thereof and is preferably dicyclohexylmethane-4,4'-diisocyanate.

[0009] The base which is used to adjust the pH may be an alkali hydroxide such as lithium hydroxyde, sodium hydroxyde, potassium hydroxide, or a trialkylamine or a trialkylamine containing hydroxyl functions. Optionally, the base or part of the base may be incorporated in the polycarbodiimide chain by capping the polycarbodiimide chain with a dialkylaminoalkyl-amine or alcohol, and/or by the addition of 0.01-0.3 equivalents regarding to the diisocyanate of a tertiary amine containing polyol or polyamine during or after the polycarbodiimide formation.

[0010] A buffer may be used to fix the pH value. Useful buffers are those with an effective pH range between 11 and 14.

[0011] The compound containing a hydrophilic group and one or more amine and/or hydroxyl functions is a polyethoxy mono- or diol, a polyethoxy/polypropoxy mono- or diol, a polyethoxy mono- or diamine, a polyethoxy/polypropoxy mono- or diamine, a diol or diamine with a polyalkoxy side chain, an hydroxy- or amine alkylsulfonate, or a dialkylaminoalkyl-alcohol or amine.

[0012] The polycarbodiimide dispersions of the invention may be used as a crosslinker for carboxylic group containing resins in a conventional way: a coating mixture comprising the polycarbodiimide dispersion of the invention and an aqueous resin containing carboxylic acid functions, is prepared. The material is cured by applying the coating mixture to a substrate, for example leather or artificial leather, and evaporating the water. Many additional ingredients may be present, for example fillers, colorants, pigments, silicons, surfactants and the like.

[0013] For several applications it is advantageous when the distance between the carbodiimide functions in the molecule is increased. In this way the crosslinking is less rigid, the coatings will be more flexible and problems such as greying, which is an effect that the coating is turning greyish and mat at stretching, or brittleness of the coatings may be prevented. Therefore flexible segments may be incorporated in the polycarbodiimide chain as a "spacer" to separate the carbodiimide functions. For this interest 0.01-0.30 equivalents of a mono- or polyol or a mono- or polyamine regarding to the polyisocyanate are added before, during or after the polycarbodiimide formation, which polyol or polyamine is for example a mono or polyhydroxy-alkane, a polyether mono-or polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactam polyol, a mono- or polyamino-alkane, a polyether mono-or polyamine.

[0014] The polycarbodiimide dispersions of the invention have several advantages: - the dispersions are stable - the polycarbodiimide is an aqueous dispersion and can be easily mixed with an aqueous resin containing carboxylic acid functions - the products are solvent free and no volatile organic vapours escape during the application - the carbodiimide formation with 4,4'-dicyclohexylmethylene diisocyanate (and isophorone diisocyanate) with 1-methylphospholene-1-oxide as carbodiimide catalyst takes less extreme conditions than the procedure with the diisocyanates described in US 5688875 and US 5859166.

Examples

Examples 1A-1F

[0015] The preparation of aqueous dispersions of polycarbodiimides based on dicyclohexylmethane-4,4'-diisocyanate.

[0016] Under a nitrogen atmosphere 262 g of dicyclohexylmethane-4,4'-diisocyanate (in the following indicated as HMDI) and 4 g of 1-methylphospholene-1-oxide were heated while stirring to 140°C and heating was continued until an isocyanate content of 8.20 was obtained. Then the mixture was cooled to 90-100°C. The reaction time was 8 hrs. Hydrophilic compounds were added as indicated in Table 1. 0.01 weight % of dibutyl tin laureate was added as a catalyst when hydroxy functional hydrophilic compounds were used and the mixtures were reacted further at 90-100°C until the NCO-signal in the IR-spectrum was disappeared. In the case of Example 1E the amine functional compound was added after 1 hr of reaction time. The mixtures were cooled down to 60-65°C and dispersed in water of 60-65°C while the solids amount was adjusted to 35 %. In the case of Example 1F the amine functional compound was added to the dispersion afterwards and the mixture was stirred for 10 min. A 10 % solution of a base in water as presented in Table 1 was added until the pH was 11-12. The samples were subjected to a stability test at 50°C. Every 2 weeks the carbodiimide amount was checked. The products were stable for at least 8 weeks at 50°C.

Table 1

No	Hydrophilic hydroxy functional compounds I and II	Weight amounts of compounds I and II (g)	Base used to adjust the pH
1A	M-PEG-350[a)]	158.67	sodium hydroxide
1B	M-PEG-350	158.67	triethanolamine
1C	M-PEG-350	158.67	ammonia
1D	M-PEG-350 + DMEA[b)]	79.33 + 20.17	sodium hydroxide
1E	M-PEG-350 + methoxyethylamine	119.00 + 8.50	sodium hydroxide
1F	M-PEG-350 + Na-taurine[c)]	79.33 + 33.32	sodium hydroxide
a) M-PEG-350 is a polyethoxy ethanol with a mean molecular weight of 350 b) DMEA is N-dimethylethanolamine c) Na-taurine is sodium 2-aminoethylsulfonate			

Examples 2A-2G

[0017] The preparation of aqueous dispersions of polycarbodiimides based on HMDI.

[0018] The examples of example 1A-1F were repeated with the exception that the water was replaced by a 0.01 M disodiumphosphate buffer solution. The samples were subjected to a stability test at 50°C. Every 2 weeks the carbodiimide amount was checked. The products were stable for at least 8 weeks at 50°C.

Example 3

[0019] The preparation of an aqueous dispersion of a polycarbodiimide based on HMDI.

[0020] The example of 1 A was repeated with the exception that 15 g of butanediol was added to the diisocyanate before the catalyst for the carbodiimide formation was added. The reaction was continued until an isocyanate content of 7.01 was obtained and the amount of M-PEG was 148.61 g.

Example 4

[0021] The preparation of an aqueous dispersion of a polycarbodiimide based on HMDI.

[0022] Under a nitrogen atmosphere 262 g of HMDI and 4 g of 1-methylphospholene-1-oxide were heated while stirring to 140°C and heating was continued until an isocyanate content of 14.26 was obtained and the mixture was cooled to 90°C. Polyols were added as presented in Table II plus 0.01 weight % of dibutyl tin laureate. Stirring was continued for 30 min at 90°C and 147 g of M-PEG-350 was added. Stirring was continued at 90°C till no NCO-signal was observed in the IR-spectrum. The mixtures were cooled down to 60-65°C and dispersed in water of 60-65°C while the solids amount was adjusted to 40 %. A 10 % solution of NaOH in water was added until the pH was 11. The sample was subjected to the stability test as mentioned above. The products were stable for at least 8 weeks at 50°C.

Table II

No	Polyol	Weight amount of the spacer (g)
4A	ethyleneglycol	12.4
4B	1,6-hexanediol	23.6
4C	triethylene glycol	30.0
4D	PPG-425[a)]	85.0
a) PPG-425 is a propyleneglycol with a mean molecular weight of 425		

Example 5

[0023] The preparation of aqueous dispersions of polycarbodiimides based on diphenylmethane-4,4'-diisocyanate.

[0024] Under a nitrogen atmosphere 150 g of diphenylmethane-4,4'-diisocyanate and 140 g M-PEG-350 were heated to 80°C and the mixture was stirred for 60 min at 80°C. 0,4 g of 1-methylphospholene-1-oxide was added and heated and stirring at 80°C was continued until the NCO-signal in the IR-spectrum was disappeared. The reaction time was 3 hrs. The mixtures were cooled down to 60-65°C and dispersed in water of 60-65°C while the solids amount was adjusted to 40 %. 5 % Of a 1 molar solution of sodium carbonate in water was added and the obtained mixture was stirred until homogenous and then a 10% solution of sodium hydroxyde in water was added until the pH was 11-12.

Claims

1. A process for the preparation of stable aqueous polycarbodiimide dispersions, to be used as crosslinking agent, which are free of organic solvents, **characterised in**:

- reacting a polyisocyanate in the presence of a carbodiimide catalyst to form a polycarbodiimide,
- terminating and/or chain extending the polycarbodiimide chain by the addition of a compound containing a hydrophilic group and one or more amine and/or hydroxy functions during or after the polycarbodiimide formation
- dispersion of the resulting compound in water, wherein the pH is adjusted to a value between 11 and 14 by the addition of a base and/or a buffer to the water used for the dispersion and/or to the obtained aqueous dispersion.

2. A process according to claim 1, **characterised in that** said terminating or chain extending with the compound containing a hydrophylic group and one or more amine functions occurs during or after the dispersion of the polycarbodiimide in water.

3. A process according to claims 1 and 2, **characterised in that** the pH of the polycarbodiimide dispersions is adjusted to a value between 11 and 13.

4. A process according to claims 1 - 3, **characterised in that** said carbodiimide-forming catalyst is 1-methylphospholene-1-oxide.

5. A process according to claims 1-4 in which the polyisocyanate which is used to prepare the polycarbodiimide is toluene-2,4- diisocyanate, toluene-2,6-diisocyanate and mixtures thereof, diphenylmethane-4,4'-diisocyanate, 1,4-phenylenediisocyanate, dicyclohexylmethane-4,4'diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, 1,6-hexyldiisocyanate, 1,4-cyclohexyldiisocyanate , norbonyldiisocyanate, or a mixture thereof.

6. A process according to claims 1 - 5, **characterised in that** the polyisocyanate is dicyclohexylmethane-4,4'-diisocyanate.

7. A process according to claims 1 - 6, **characterised in that** said base is an alkali hydroxyde such as lithium hydroxyde, sodium hydroxyde, potassium hydroxide, or a trialkylamine, or a trialkylamine containing hydroxy functions.

8. A process according to claims 1-7, **characterised in that** said base or part of said base is incorporated in the polycarbodiimide chain by capping the polycarbodiimide chain with a dialkylaminoalkyl-amine or alcohol, and/or by the addition of 00.1-0.3 equivalents regarding to the diisocyanate of a tertiary amine containing polyol or polyamine during or after the polycarbodiimide formation.

9. A process according to claims 1 - 8, **characterised in that** the effective pH range of the buffer is between 9 and 14.

10. A process according to claims 1-9, **characterised in that** said compound containing a hydrophilic group and one or more amine and/or hydroxy functions is a polyethoxy mono- or diol, a polyethoxy/polypropoxy monoor diol, a polyethoxy mono- or diamine, a polyethoxy/polypropoxy mono- or diamine, a diol or diamine with a polyalkoxy side chain, an hydroxy- or amine alkylsulfonate, or a dialkylaminoalkyl- alcohol or amine, or a mixture thereof.

11. A process according to claims 1 - 10, **characterised in that** 0.01-0.30 equivalents of a mono- or polyol or a mono- or polyamine regarding to the polyisocyanate are added in addition before, during or after the polycarbodiimide formation, which polyol or polyamine is for example a mono-or polyhydroxy-alkane, a polyether mono- or polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactam polyol, a mono- or polyamino-alkane, a polyether mono- or polyamine.

12. A coating mixture comprising the polycarbodiimide dispersions obtained according to claims 1-11 as crosslinking agent and an aqueous resin containing carboxylic acid functions.

Patentansprüche

1. Verfahren zur Herstellung stabiler wässriger Polycarbodiimiddispersionen, die, frei von organischen Lösungsmitteln , als Vernetzungsmittel verwendet werden, **gekennzeichnet durch**:

- Reagieren eines Polyisocyanats in Gegenwart eines Carbodiimidkatalysators, um ein Polycarbodiimid zu bilden,
- Beenden und/oder Kettenverlängerung der Polycarbodiimidkette durch Hinzufügen einer Verbindung, die eine hydrophile Gruppe und eine oder mehrere Amin- und/oder Hydroxyfunktionen enthält, während oder nach der Polycarbodiimidbildung.
- d Dispergieren der resultierenden Verbindung in Wasser, wobei der pH durch Hinzufügen einer Base und/oder eines Puffers zu dem für das Dispergieren verwendete Wasser und/oder zu der erhaltenen wässrigen Dispersion auf einen Wert zwischen 11 und 14 angepasst wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Beenden oder die Kettenverlängerung mit der Verbindung, die eine hydrophile Gruppe und eine oder mehrere Aminfunktionen enthält, während oder nach dem Dispergieren des Polycarbodiimids in Wasser erfolgt.

3. Verfahren nach den Ansprüchen 1 und 2, **dadurch gekennzeichnet, dass** der pH-Wert der Polycarbodiimiddispersionen auf einen Wert zwischen 11 und 13 angepasst wird.

4. Verfahren nach den Ansprüchen 1-3, **dadurch gekennzeichnet, dass** der Carbodiimid-bildende Katalysator 1-Methylphospholen-1-oxid ist.

5. Verfahren nach den Ansprüchen 1-4, bei dem das Polyisocyanat, das zur Herstellung des Polycarbodiimids verwendet wird, Toluen-2,4-diisocyanat, Toluen-2,6-diisocyanat und Gemischen davon, Diphenylmethan-4,4'-diisocyanat, 1,4-Phenylendiisocyanat, Dicyclohexylmethan-4,4'-diisocyanat, 3-Isocyanatmethyl-3,5,5-trimethylcyclohexylisocyanat, 1,6-Hexyldiisocyanat, 1,4-Cyclohexyldiisocyanat, Norbonyldiisocyanat oder ein Gemisch davon ist.

6. Verfahren nach den Ansprüchen 1-5, **dadurch gekennzeichnet, dass** das Polyisocyanat Dicyclohexylmethan-4,4'-diisocyanat ist.

7. Verfahren nach den Ansprüchen 1-6, **dadurch gekennzeichnet, dass** die Base ein Alkalihydroxid, wie beispielsweise Lithiumhydroxid, Natriumhydroxid, Kaliumhydroxid oder ein Trialkylamin oder ein Hydroxyfunktionen enthaltendes Trialkylamin, ist.

8. Verfahren nach den Ansprüchen 1-7, **dadurch gekennzeichnet, dass** die Base oder ein Teil der Base durch Capping der Polycarbodiimidkette mit einem Dialkylaminalkylamin oder -alkohol und/oder durch Hinzufügen von 00,1 bis 0,3 Äquivalenten, bezogen auf das Diisocyanat, eines tertiären Aminhaltigen Polyols oder Polyamins während oder nach der Polycarbodiimidbildung in die Polycarbodiimidkette eingebaut wird.

9. Verfahren nach den Ansprüchen 1-8, **dadurch gekennzeichnet, dass** der wirksame pH-Wert-Bereich des Puffers zwischen 9 und 14 liegt.

10. Verfahren nach den Ansprüchen 1-9, **dadurch gekennzeichnet, dass** die Verbindung, die eine hydrophile Gruppe und eine oder mehrere Amin- und/oder Hydroxyfunktionen enthält, ein Polyethoxymono- oder -diol, ein Polyethoxy/Polypropoxymono- oder -diol, ein Polyethoxymono- oder -diamin, ein Polyethoxy/Polypropoxymono- oder -diamin, ein Diol oder Diamin mit einer Polyalkoxy-Seitenkette, ein Hydroxy- oder Aminalkylsulfonat oder ein Dialkylaminalkylalkohol oder -amin oder ein Gemisch davon ist.

11. Verfahren nach den Ansprüchen 1-10, **dadurch gekennzeichnet, dass** 0,01-0,30 Äquivalente eines Mono- oder Polyols oder eines Mono- oder Polyamins, bezogen auf das Polyisocyanat, zusätzlich vor, während oder nach der Polycarbodiimidbildung hinzugefügt werden, wobei das Polyol oder Polyamin beispielsweise ein Mono- oder Polyhydroxyalkan, ein Polyethermono- oder -polyol, ein Polyesterpolyol, ein Polycarbonatpolyol, ein Polycaprolactampolyol, ein Mono- oder Polyaminalkan, ein Polyethermono- oder -polyamin ist.

12. Beschichtungsgemisch, umfassend die Polycarbodiimiddispersionen, erhalten nach den Ansprüchen 1-11 als Vernetzungsmittel, und ein wässriges Harz, das Carboxylsäurefunktionen enthält.

Revendications

1. Procédé de préparation de dispersions de polycarbodiimide aqueuses stables, à utiliser en tant qu'agent de réticulation, qui sont dépourvues de solvants organiques, **caractérisé par** :

   - la réaction d'un polyisocyanate en présence d'un catalyseur de carbodiimide pour former un polycarbodiimide,
   - la terminaison et/ou l'extension de la chaîne de polycarbodiimide par l'addition d'un composé contenant un groupe hydrophile et une ou plusieurs fonctions amine et/ou hydroxy pendant ou après la formation du polycarbodiimide
   - la dispersion du composé résultant dans l'eau, dans lequel le pH est ajusté à une valeur comprise entre 11 et 14 par l'addition d'une base et/ou d'un tampon à l'eau utilisée pour la dispersion et/ou à la dispersion aqueuse obtenue.

2. Procédé selon la revendication 1, **caractérisé en ce que** ladite terminaison ou extension de chaîne avec le composé contenant un groupe hydrophile et une ou plusieurs fonctions amine se produit pendant ou après la dispersion du polycarbodiimide dans l'eau.

3. Procédé selon les revendications 1 et 2, **caractérisé en ce que** le pH des dispersions de polycarbodiimide est ajusté à une valeur comprise entre 11 et 13.

4. Procédé selon les revendications 1 à 3, **caractérisé en ce que** ledit catalyseur de formation de carbodiimide est du 1-méthylphospholène-1-oxyde.

5. Procédé selon les revendications 1 à 4 dans lequel le polyisocyanate qui est utilisé pour préparer le polycarbodiimide est du toluène-2,4-diisocyanate, du toluène-2,6-diisocyanate et des mélanges de ceux-ci, du diphénylméthane-4,4'-diisocyanate, du 1,4-phénylènediisocyanate, du dicyclohexyl-méthane-4,4'-diisocyanate, du 3-isocyanatométhyl-3,5,5-triméthylcyclohexylisocyanate, du 1,6-hexyldiisocyanate, du 1,4-cyclohexyldiisocyanate, du norbonyldiisocyanate, ou un mélange de ceux-ci.

6. Procédé selon les revendications 1 à 5, **caractérisé en ce que** le polyisocyanate est du dicyclohexylméthane-4,4'-diisocyanate.

7. Procédé selon les revendications 1 à 6, **caractérisé en ce que** ladite base est un hydroxyde alcalin tel que de l'hydroxyde de lithium, de l'hydroxyde de sodium, de l'hydroxyde de potassium, ou une trialkylamine, ou une trialkylamine contenant des fonctions hydroxy.

8. Procédé selon les revendications 1 à 7, **caractérisé en ce que** ladite base ou une partie de ladite base est incorporée dans la chaîne de polycarbodiimide en coiffant la chaîne de polycarbodiimide avec une dialkylaminoalkylamine ou un alcool, et/ou par l'addition de 00,1 à 0,3 équivalent par rapport au diisocyanate d'une amine tertiaire contenant un polyol ou une polyamine pendant ou après la formation du polycarbodiimide.

9. Procédé selon les revendications 1 à 8, **caractérisé en ce que** la gamme de pH effectif du tampon est comprise entre 9 et 14.

10. Procédé selon les revendications 1 à 9, **caractérisé en ce que** ledit composé contenant un groupe hydrophile et une ou plusieurs fonctions amine et/ou hydroxy est un polyéthoxy mono- ou diol, un polyéthoxy/polypropoxy mono- ou diol, une polyéthoxy mono- ou diamine, une polyéthoxy/polypropoxy mono- ou diamine, un diol ou une diamine comportant une chaîne latérale polyalcoxy, un hydroxy- ou amino alkylsulfonate, ou un(e) dialkylaminoalkyl-alcool ou amine, ou un mélange de ceux-ci.

11. Procédé selon les revendications 1 à 10, **caractérisé en ce que** de 0,01 à 0,30 équivalent d'un mono- ou polyol ou d'une mono- ou polyamine par rapport au polyisocyanate est en outre ajouté avant, pendant ou après la formation du polycarbodiimide, lequel polyol ou laquelle polyamine est par exemple un mono- ou polyhydroxy-alcane, un polyéther mono- ou polyol, un polyester polyol, un polycarbonate polyol, un polycaprolactame polyol, un mono- ou polyamino-alcane, une polyéther mono- ou polyamine.

12. Mélange de revêtement comprenant les dispersions de polycarbodiimide obtenues selon les revendications 1 à 11 en tant qu'agent de réticulation et une résine aqueuse contenant des fonctions acide carboxylique.

REFERENCES CITED IN THE DESCRIPTION

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- EP 0686626 A **[0001] [0003]**
- US 5859166 A **[0001] [0014]**
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- US 6127029 A **[0002]**
- US 6127477 A **[0002]**
- US 6248819 B1 **[0003]**
- EP 878496 A **[0007]**